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Published in:
Materials Research Bulletin

DOI:
10.1016/S0025-5408(01)00663-8

Pergamon

Materials Research Bulletin 36 (2001) 1837–1845

Materials Research Bulletin

The preparation of a novel layered lead titanate and its conversion to the perovskite lead titanate $PbTiO_3$

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(Refereed)
Received 30 January 2001; accepted 10 April 2001

Abstract

A novel layered lead titanate with the approximate composition $PbTiO_2(CO_3)_{0.3}(NO_3)_{0.35}(OH)$ has been synthesized hydrothermally under acidic conditions. The structure has been solved and refined from X-ray and neutron powder diffraction data in the space group P -3 1 m, with cell dimensions a = 5.1787(5) Å and c = 8.5222(7) Å. The titanate layers possess a gibbsite-like structure: lead cations and oxyanions such as carbonate and nitrate are included between the layers. Upon heating the solid loses water, carbon dioxide and nitrogen dioxide and converts via a poorly crystalline intermediate phase to the perovskite $PbTiO_3$. The conversion is complete by 550°C; continued heating results in an increase in crystallinity.

Keywords: A. Layered compound; B. Hydrothermal synthesis; C. X-ray and neutron diffraction

1. Introduction

Lead titanate, $PbTiO_3$, and the related lead zirconate titanate (PZT) and lead lanthanum zirconate titanate (PLZT), are among the most widely exploited of all piezoelectric ceramics [1]. Synthesis of lead titanate via conventional solid-state mixing and heating is usually only possible at temperatures at which loss of volatile lead becomes a problem. As a result, the preparation of the ceramic perovskite at relatively low temperatures either directly or from

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0025-5408/01/$ – see front matter
PII: S0025-5408(01)00663-8

Table 1
Atomic coordinates for $PbTiO_2(CO_3)_{0.3}$ $(NO_3)_{0.35}(OH)$ determined from neutron powder diffraction

Atom	x	y	z	Occ.	B_{iso}
Pb1	0.0000	0.0000	0.2198(6)	1	2.29(11)
Ti1	0.3333	0.6667	0.5000	1	0.68(12)
O1	0.0000	0.3707(5)	0.3715(4)	1	0.55(4)
O2	0.5202(20)	0.4798(20)	0.0000	0.35(2)	2.7(4)
C1[a]	0.3333	0.6667	0.0000	0.43(3)	1.03(20)

[a] C1 is assumed to contain carbon and nitrogen in a ratio of 1:1. The average scattering length was used to calculate the fractional occupancy

precursors such as mixed alkoxides [2] is of ongoing interest. Hydrothermal experiments in the PbO-TiO_2 system, working on the Pb-rich side of the system and at conditions of alkaline pH (11.4–14.2) have previously been reported to give lead titanate perovskite directly [3]. Other groups have reported a microporous lead titanate phase of unidentified structure [4,5] to be prepared hydrothermally at low pH. We report here the synthesis and structure elucidation of a novel lead- and titanium-containing layered solid with oxyanions located between the titanate layers. The solid is found to convert to lead titanate perovskite upon heating in air.

2. Experimental

The title compound was prepared as part of a program examining the hydrothermal synthesis of titanates. A gel of composition 1.7 $Pb(NO_3)_2$:1.0 $Ti(OBt)_4$:0.95 TPAOH:50 H_2O was prepared in two steps. First, titanium butoxide was allowed to hydrolyze in water and then dissolved in a 10 wt% aqueous solution of tetrapropylammonium hydroxide. In the second step, a solution of lead nitrate was added, giving rise to a white gel, which had a starting pH of 2.5. This gel was heated in a sealed PTFE-lined autoclave at 190°C for 7 days, and the product filtered and dried. Experiments were also performed varying the lead nitrate:titanium ratio to 1:1 and changing the alkylammonium base (to tetramethylammonium, tetrapropylammonium, and tetrabutylammonium hydroxides). Also, the lead nitrate was replaced with lead acetate to determine the role of pH, because this gave a starting pH of 5.5.

X-ray diffraction was performed on a STOE STADIP diffractometer using monochromated Cu $K_{\alpha 1}$ radiation. The sample was loaded into a 0.5-mm glass capillary, and the measurement made in Debye-Scherrer geometry. Neutron powder diffraction was performed on station POLARIS at the ISIS spallation neutron source at the Rutherford Laboratory. The sample used for neutron diffraction was heated overnight in an excess of deuterium oxide to reduce incoherent scattering from H atoms.

Transmission electron microscopy and electron diffraction were performed on the as-prepared material using a JEOL 2010 microscope. Selected-area EDX analysis was performed on the sample before and after calcination to 900°C on the same instrument. Carbon,

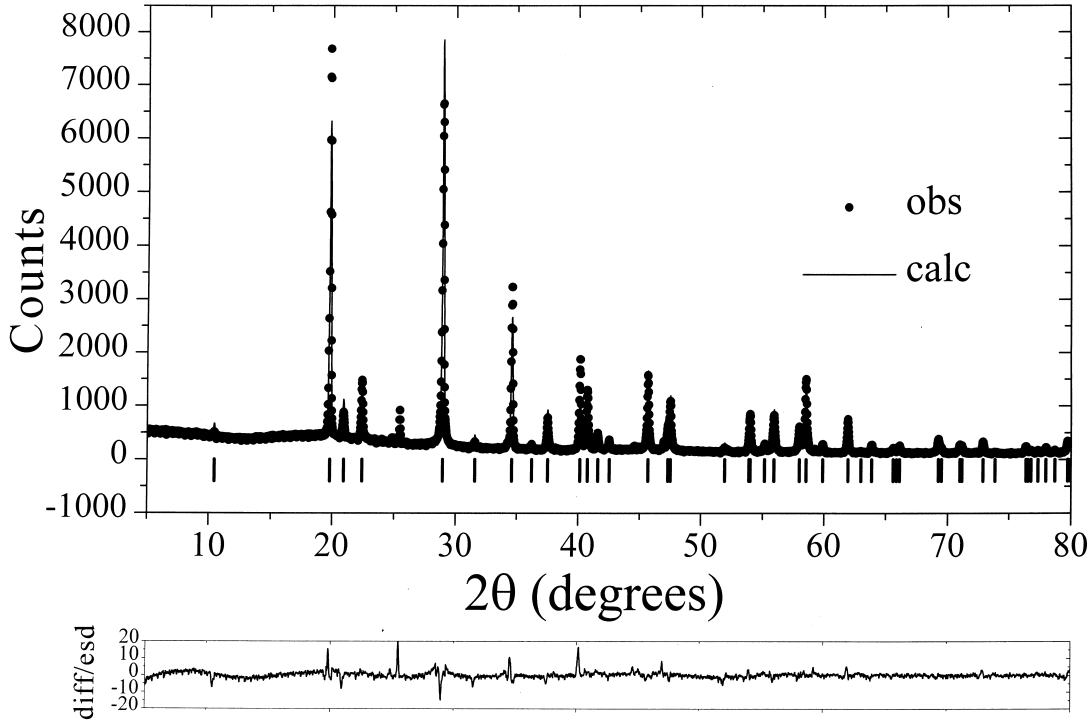

Fig. 1. X-ray powder diffraction pattern of the new lead titanate mixed oxyanion phase. The profile is matched by a Rietveld refinement that uses atomic coordinates derived from neutron powder diffraction (see later). (R_{wp} = 10.8%, R_p = 8.2%, R_{ex} = 5.58%, χ^2 = 3.79 for 15 parameters).

hydrogen, and nitrogen analysis was also performed on the as-prepared solid. TGA of the sample was performed at 10°C/min in air to 600°C. TG-MS was also performed to identify the gases evolved during heating over this temperature range. Portions of the original solid were then heated isothermally in air for 8 h at temperatures of 250, 350, 400, 450, 500, 550, and 900°C and the X-ray diffraction pattern collected for each sample.

3. Results and discussion

A novel lead and titanium phase, with a characteristic X-ray diffraction pattern, is obtained by hydrothermal treatment of a gel prepared from tetrabutyl titanate, tetraethylammonium hydroxide, and lead nitrate in the ratio 1.0 $Ti(OBt)_4$:0.95 TPAOH:1.7 $Pb(NO_3)_2$:50 H_2O at an acidic initial pH of 2.5. The same material is also formed using tetrapropylammonium hydroxide in place of tetraethylammonium hydroxide, but not with tetramethyl or tetrabutylammonium hydroxides, when lead carbonate and other, poorly crystalline, phases are formed. Neither is a crystalline phase formed if the starting pH is raised to 5.5 by replacing lead nitrate with lead acetate in the synthesis.

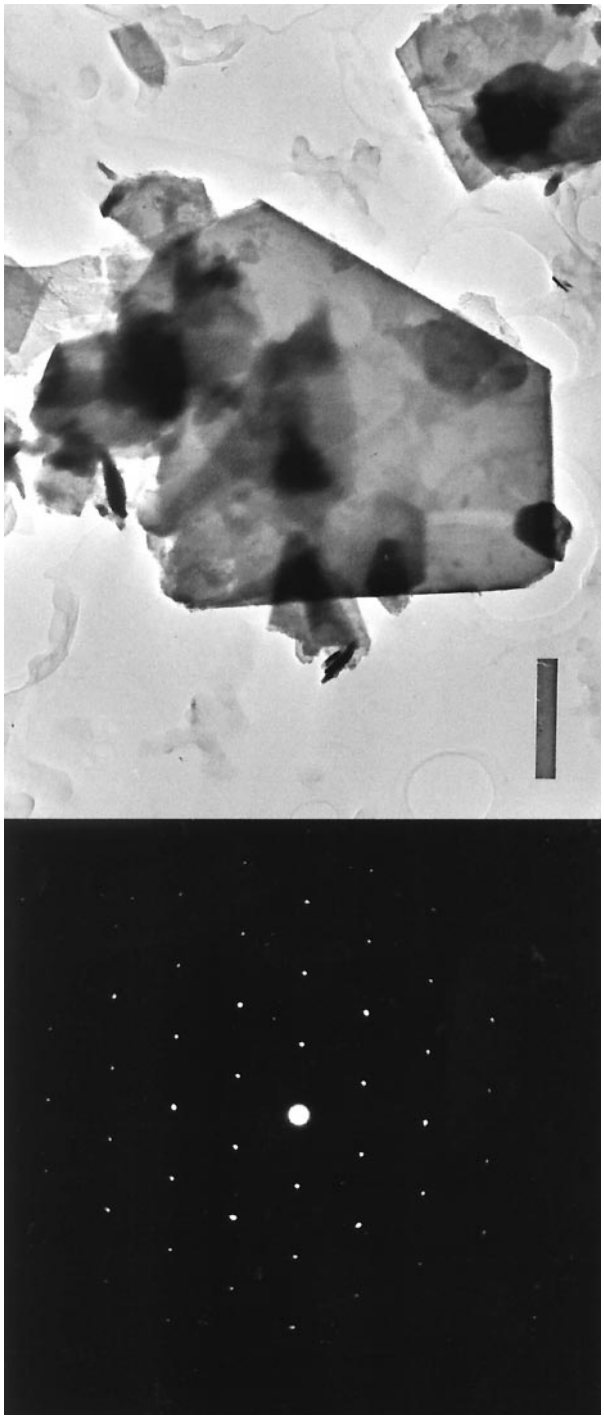

Fig. 2. Transmission electron micrograph (1 μm scale bar marked) and electron diffraction pattern (down the [001] axis) of particles of the as-prepared lead titanate, taken with the incident beam perpendicular to the platelets.

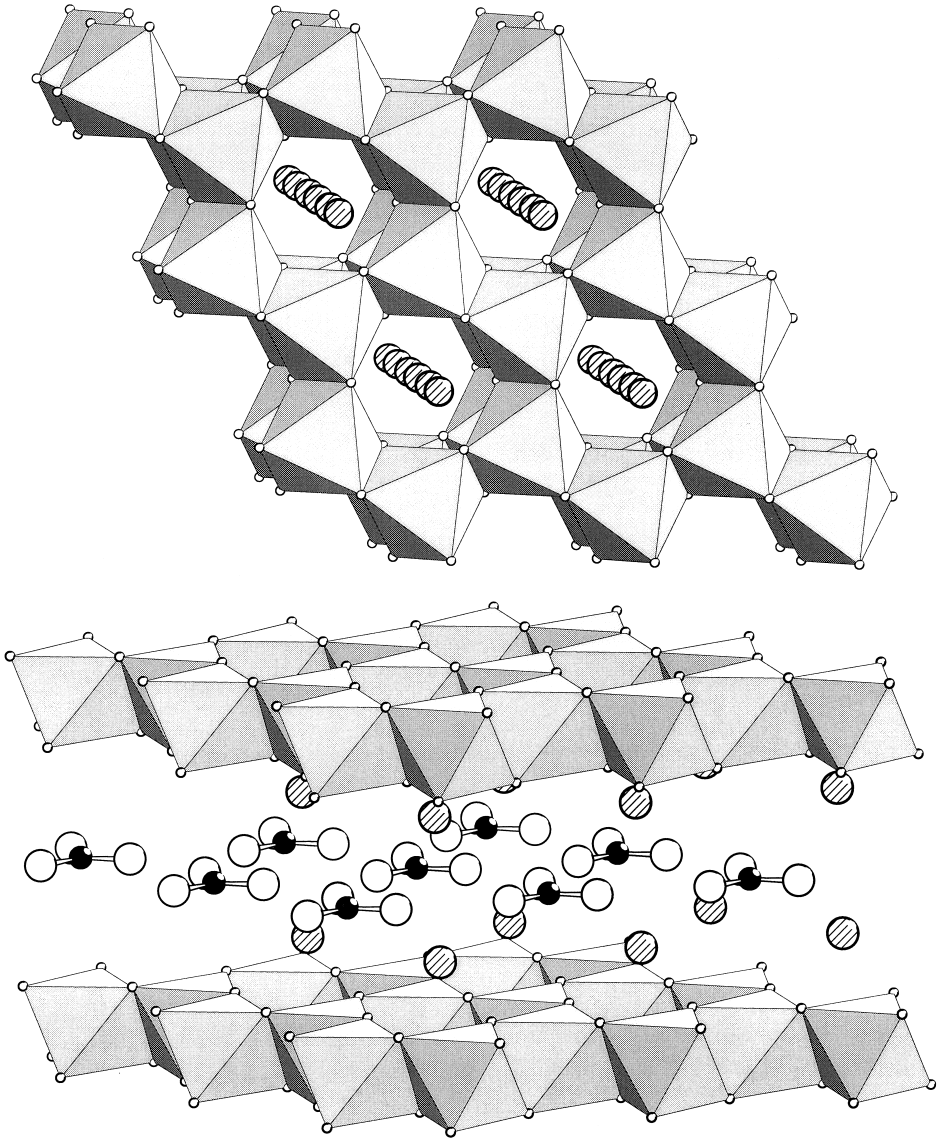

Fig. 3. The structure of the lead titanate precursor, (a) viewed along c, and showing the position of the titanate layers and the Pb^{2+} cations (hatched) and (b) viewed perpendicular to the c axis, showing the layers of titanate octahedra, separated by two layers of lead cations and a disordered layer of carbonate and nitrate anions between them. The oxyanions show partial occupancy in the structure, and in the figure are drawn in one of the two possible configurations.

The as-synthesised lead titanate product is highly crystalline, as shown by the powder X-ray diffraction pattern (Fig. 1). Electron microscopy and electron diffraction (Fig. 2) reveal that the sample is composed of platelets with a trigonal or hexagonal symmetry axis perpendicular to the plane of the platelets. EDX analysis showed the material to contain lead, titanium, and oxygen in the approximate ratio of 1:1:6.

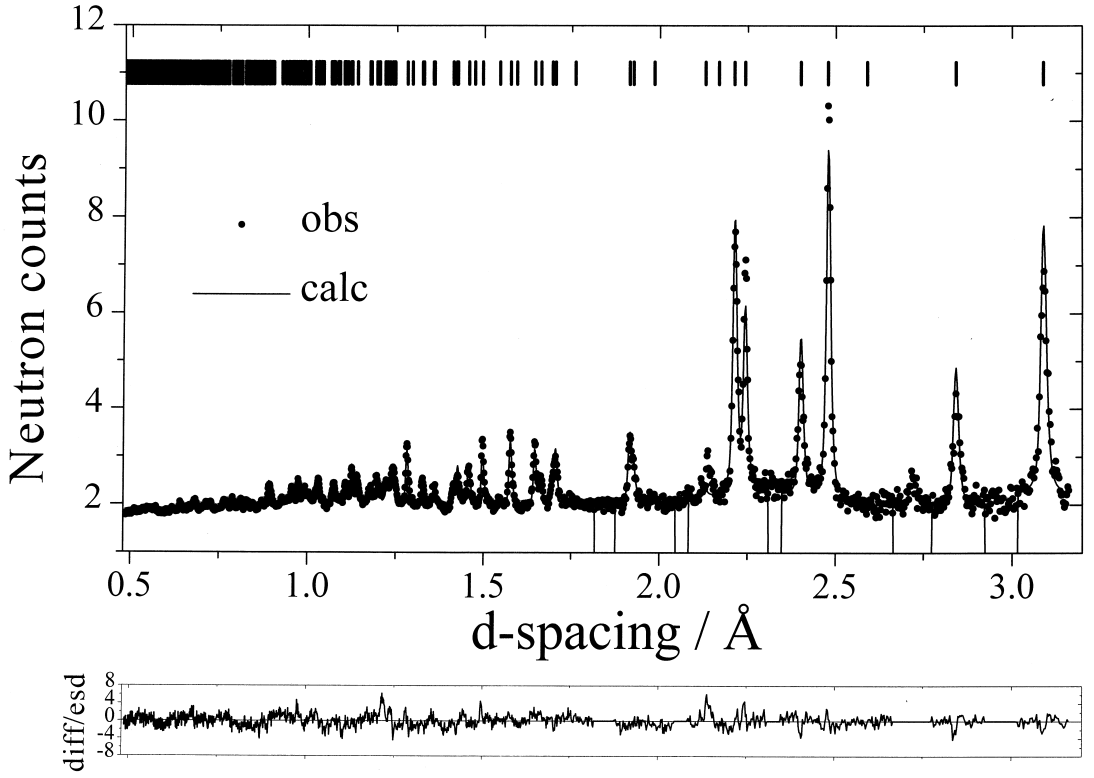

Fig. 4. Neutron powder diffraction data and profile refinement of the lead titanate mixed oxyanion phase, showing excluded regions, reflection positions and difference profile. (R_{wp} = 2.29%, R_p = 3.2%, R_{ex} = 1.7%, χ^2 = 1.9 for 26 variables).

Upon heating in air, the sample gives a total weight loss of 12.8% in three equal steps. The first two steps of weight loss partly overlap, and occur mainly between 250 and 340°C, and the third occurs mainly between 400 and 480°C, so that an intermediate phase must be formed between 340 and 400°C. TG-MS indicates that the first peak is made up of at least two events. Deconvolution of the MS traces indicates that the first event corresponds to a simultaneous loss of water, triethylamine, and some nitrogen oxides, whereas the second event corresponds to a loss of carbon dioxide. The third event, which is quite separate, can be assigned unequivocally to nitrogen dioxide. The result of heating the phase at elevated temperatures is identified by X-ray diffraction to be $PbTiO_3$. Elemental analysis reveals the sample contains 1.98 wt% C, 0.3 wt% H and 1.69 wt% N. The as-prepared phase is, therefore, a lead titanate containing carbonate, nitrate, and hydroxide ions, with approximate composition Pb Ti O_2 $(CO_3)_{0.3}$ $(NO_3)_{0.35}$ (OH), estimated from a combination of inorganic analysis, CHN analysis, and TGA and TG-MS.

The X-ray pattern of the as-synthesised material was indexed with the help of the indexing program VISSER to be based on a hexagonal unit cell, with a = 5.19 Å and c = 8.51 Å. Minor amounts of an impurity were present. An initial study of the known phases indicates the a repeat is that expected for structures based on close packed oxygen layers, and the

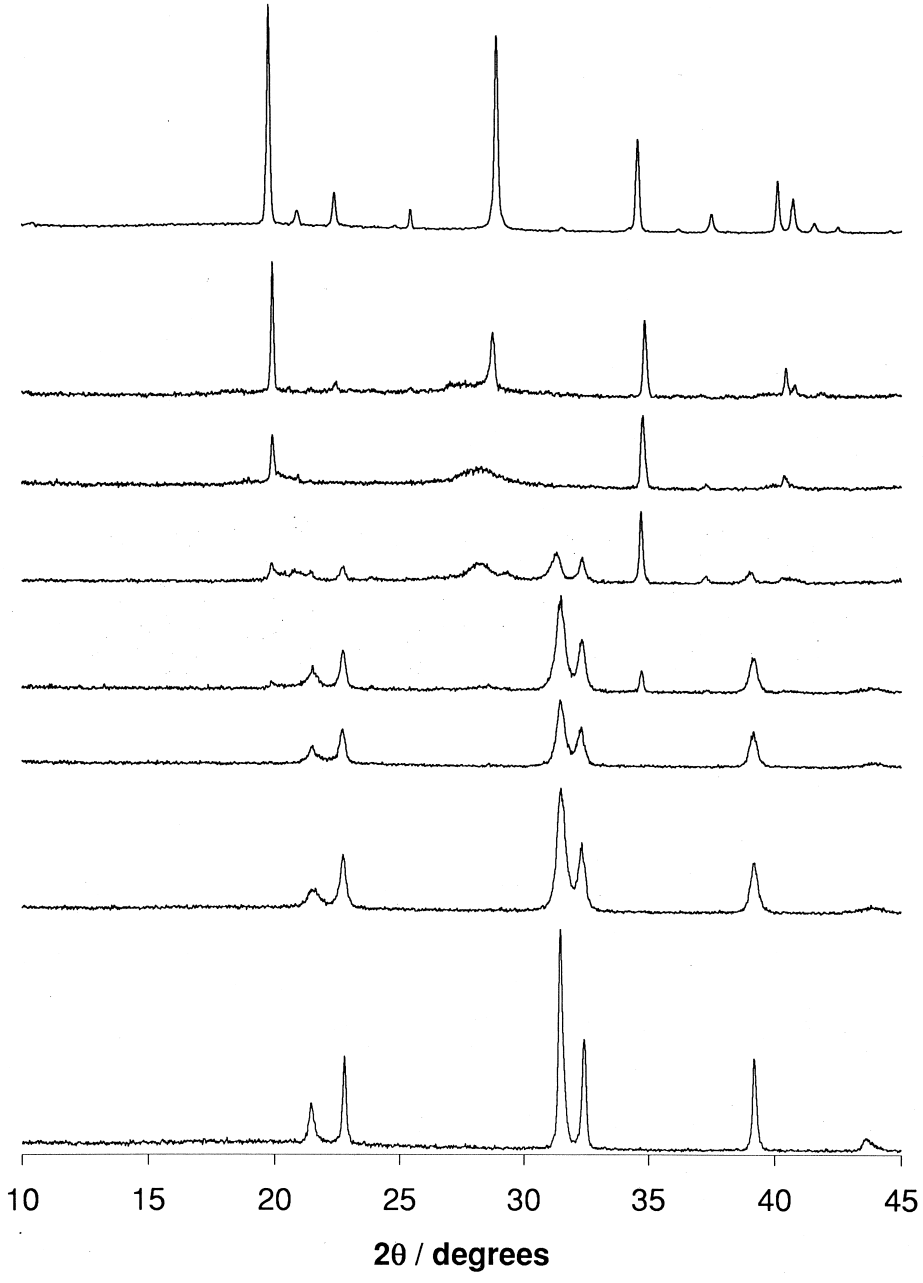

Fig. 5. X-ray diffraction profiles of the lead titanate precursor (top) heated for 8 h at temperatures of (from second top to bottom) 250, 350, 400, 450, 500, 550, and 900°C, showing topotactic conversion to the lead titanate perovskite, $PbTiO_3$.

X-ray intensities are matched approximately by two lead atoms in the unit cell, with x = y = 0 and a z separation of around 0.5. The unit cell composition is therefore estimated as $Pb_2Ti_2O_4(CO_3)_{0.6}(NO_3)_{0.7}$ $(OH)_2$. The X-ray pattern is dominated by scattering from the

lead atoms so that neutron data was obtained to locate the oxygen and titanium. The structural model from the neutron and X-ray data was refined in the space group P -3 1 m and the lead, titanium, and most of the oxygens have been located, along with disordered carbon and nitrogen. The titanium and a fully occupied oxygen position were found to make up a layer of edge-sharing TiO_6 octahedra and the lead cations were found to occur in two layers between these titanate sheets (Fig. 3a). Additional scattering from the interlayer region, between the two layers of lead cations, was refined in two positions (1/3, 2/3, 0) and (0, 1/2, 0) with partial occupancies. The distance between these is around 1.5 Å, and is closer to C—O and N—O bond-lengths of the carbonate and nitrate species (expected at 1.3 Å) than to O—O bond lengths. The scattering was, therefore, attributed to nitrate or carbonate species disordered between the layers. Examination of the arrangement suggests that the C/N atoms can only be present at 50% occupancy, and that O2 should be displaced off the mirror plane closer to C1 (the carbon or nitrogen) (Fig. 3b). The refined position of O2 gives a C—O bond distance of 1.3 Å. The fit to the the neutron powder diffraction data is illustrated in Fig. 4, and the structural details are given in Table 1. The high thermal parameter of the interlayer oxygen, O2, is likely to result from associated disorder of nitrate and carbonate ions, of which it is a part. This interlayer disorder may contribute to the relatively high thermal parameter of the lead atom, and it is possible that the lead is locally displaced from its special position.

The fundamental structural unit is a layer of titanium ions sandwiched between two sheets of close-packed oxygens. The layers may be regarded as built up of distorted TiO_6 octahedra linked by sharing edges. A similar structural unit is found in gibbsite, where aluminium ions occupy two-thirds of the available interstices between two close packed oxygen layers. Above and below the layer of TiO_6 octahedra are two layers of Pb^{2+} cations coordinated to oxygens of the titanate layer. They are also coordinated to oxygens from carbonate and nitrate ions that occupy disordered positions between the titanate layers and between the two layers of lead cations. Similar layered titanates, where the edge-sharing TiO_6 octahedra are arranged in corrugated layers, are well known [6,7], and these include a species with the same structure as boehmite [γAlO(OH)] and lepidocrocite [γFeO(OH)]. However, to our knowledge this is the first time a gibbsite-type titanate layer has been seen. Also, a lead-bearing phase, the mineral quenselite, $PbMnO_2(OH)$, adopts a layered structure consisting of layers of MO_6 octahedra with double layers of lead cations in the interlayer space, although in this structure the octahedral layer has no holes [8,9].

To follow the conversion, XRD patterns were taken after heating in air at 250, 300, 350, 400, 450, 500, 550, and 900°C (Fig. 5). After heating at 250°C the sample has lost some crystallinity, and upon heating to 300°C reflections of the form (hkl) with non-zero values of l disappear. This indicates that long-range order is lost rapidly perpendicular to the titanate sheets, while the *a*–*b* repeat remains intact. Also, the (hk0) reflections shift to higher angle, indicating a shrinkage of the *a* axis from 5.185 to 5.144 Å. As predicted from the TGA, there is evidence for the formation of an intermediate phase being formed, with minor broad peaks at d = 9.4 and 4.7 Å and a large broad peak at a d-spacing of 3.1 Å. The thermal loss of carbon dioxide occurs as a topotactic transformation, probably with the “gibbsite-like” layer of TiO_6 octahedra remaining intact.

After heating at 400°C, reflections from the $PbTiO_3$ perovskite, macedonite, appear, and after heating at 500 °C only this phase remains. After heating to 450°C and above the solids are a faint orange-yellow color, the intensity of which decreases with increasing heating temperatures. Further heating results in an increase of the size of crystalline domains, as observed from the narrowing of the diffraction peaks. The final product is then phase pure $PbTiO_3$.

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